

Dynamic charge transfer and spin-phonon interaction in high- T_c superconductorsP. Piekarz^{1,2} and T. Egami^{1,3,4}¹*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*²*Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, Kraków, Poland*³*Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA*⁴*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

(Received 5 March 2004; revised manuscript received 28 February 2005; published 31 August 2005)

The effects of the electron-phonon interaction on charge and spin dynamics are studied for the one-dimensional two-band Hubbard model by the exact diagonalization method. The parameters of the model are chosen to represent a hole-doped Cu-O system. Local charge fluctuations induced by phonons are expressed in terms of microscopic current and polarization, and it is shown that the dynamic charge transfer is strongly dependent on the phonon wave vector when the system is doped with holes. The dynamic magnetic structure factor is also found to be significantly modified by lattice distortion. In particular the lowest-energy spin excitations are greatly softened, indicating significant spin-phonon coupling. It is shown that the optical response is significantly modified as well due to coupling with the lattice over an energy range far exceeding the phonon energy. These results demonstrate the unconventional nature of the electron-phonon coupling in the strongly correlated electron systems. Its possible implications to the pairing mechanism in the cuprates are discussed.

DOI: [10.1103/PhysRevB.72.054530](https://doi.org/10.1103/PhysRevB.72.054530)

PACS number(s): 74.25.Kc, 74.25.Ha, 74.72.-h, 71.27.+a

I. INTRODUCTION

Various unusual properties of the cuprate superconductors, such as non-Fermi liquid behavior, pseudogap, spin-charge stripes, and high-temperature superconductivity, are believed to be the consequences of strong electron correlation, and the dynamics of electrons and spins have been the focus of numerous theoretical studies. However, a number of experiments, including the observation of spin-charge stripes,¹ suggest that the electron-phonon (e - p) interaction also plays an active role in the cuprates, and has to be taken into account in understanding the properties of these materials.²⁻⁴ The evidence of strong e - p coupling is provided also by the angle-resolved photoemission spectroscopy (ARPES) measurements.^{5,6} Moreover, the observation of the isotope effect on the magnetic penetration depth,^{7,8} and the phonon anomaly that is closely related to the superconducting order parameter⁹ suggest that the phonon may be playing some active role in the superconductivity of the cuprates. Many other lattice effects, such as local structural instabilities,^{10,11} are also consistent with the strong electron-lattice coupling. It is possible that ionicity, covalency and strong electron correlation in the cuprates render the e - p coupling rather distinct features.¹²

The e - p coupling of materials can be characterized by the response of the electronic state to lattice deformation. In insulators, electronic states are localized and the electric charge polarization can sustain a nonzero value over a macroscopic length scale in the case of a ferroelectric solid. In contrast, in simple metals, the effects of lattice deformation on polarization are screened by delocalized charge carriers. This simple classification, however, does not adequately describe doped copper oxides. Low density of states, weak and anisotropic screening, and local spin polarization make them very different from conventional metals and very sensitive to

local lattice deformation. In particular, the optical phonons, which directly modulate the Cu—O bond distance and induce charge transfer between ions, are likely to be strongly coupled to the electronic system.^{13,14}

In order to discuss this dynamic charge transfer induced by phonons it is instructive to return to the insulating ferroelectric oxides. It is well known that the ferroelectricity of transition metal (TM) compounds, such as BaTiO₃, has a strong electronic component due to the covalency of the TM-O bond.¹⁵ As TM and O ions are displaced in space by the optical phonon mode, ionic displacements induce not only ionic polarization but also electronic polarization because of the charge transfer ΔZ . Typically the TM elements in ferroelectric oxides, such as Ti and Nb, are in the nominally d^0 configuration, but the d level is strongly hybridized with the oxygen p level. When TM ion moves closer to O, electrons are transferred from the oxygen p band to the TM d band. As a result the total polarization is equal to $P = Zu + \Delta Za$, where u is the relative ionic displacement and a is the distance between TM and O ions. Since $a/u \gg 1$, the total polarization can be much larger than the bare ionic polarization, making the Born dynamic effective charge, $Z^* = Z + \Delta Z(a/u)$, sometimes more than twice the nominal valence.^{16,17}

Since the phonons change the electron hopping integral t , they modulate the exchange interaction J , which is equal to t^2/U in the t - J model. However, if the phonon-induced charge transfer is spin polarized it can give rise to an additional spin-phonon coupling, which may be quite strong and cannot be observed in simple metals. Moreover, this kind of spin-phonon coupling, could lead to a synergetic pairing mechanism, in which both phonons and spin excitations take part as mediating bosons. The interplay of the e - p interaction and electron correlations, as well as spin-phonon effects were studied using different theoretical techniques.¹⁸⁻²² In

this paper, we use the Lanczos method, which enables us to obtain exact solutions for finite clusters with the many-body interactions, to describe the e - p coupling in terms of the wave-vector-dependent effective charge, and to demonstrate the effects of phonons on the spin dynamics and optical conductivity.

The paper is organized as follows. In Sec. II, we describe the model Hamiltonian of the CuO system. In Sec. III, we analyze the effects of the e - p interaction on charge transfer and polarization, and present the approach to study local effects in the polarization field and q -dependent properties. In Sec. IV we focus on magnetic interactions in the doped system and discuss the effect of the e - p coupling on spin dynamics. Section V presents the results of calculations of optical conductivity. Finally, discussions on the results are presented in Sec. VI.

II. MODEL

The electronic properties of the CuO₂ plane can be described within the multiband Hubbard model including the $d_{x^2-y^2}$ orbitals on Cu atoms and the $p_{x/y}$ orbitals on O atoms. Compared to one-band effective models, multiband models enable more detailed description of charge dynamics and interband effects. This is especially important for studying the bond-stretching LO phonon mode, involving primarily oxygen displacements and Cu—O charge transfer. Since the most important LO mode appears to be the one propagating along the Cu—O bond⁹ we use a one-dimensional two-band model which allows calculation with less size effect than the two-dimensional models. The Hamiltonian of the two-band Hubbard model can be written in the form

$$H = \sum_{i=1}^N [\varepsilon_i(u)n_i + U_i n_{i,\uparrow} n_{i,\downarrow} + V n_i n_{i+1}] + t_{pd}(u) \sum_{\sigma,i} (d_{i,\sigma}^\dagger p_{i+1,\sigma} + \text{H. c.}), \quad (1)$$

where i runs over all sites and N is the number of sites. Operators $d_{i,\sigma}$ and $p_{i,\sigma}$ represent the $d_{x^2-y^2}$ orbitals on coppers and p_x orbitals on oxygens, respectively. The Hamiltonian includes on-site Coulomb interactions, on copper U_d and oxygen U_p , and the nearest-neighbor (NN) intersite interaction V . For the electronic part of the model we use the standard set of parameters derived from density-functional calculations:²³ $\Delta = \varepsilon_p - \varepsilon_d = 4$, $t = 1.3$, $U_d = 8$, $U_p = 4$, $V = 1.2$ all in the units of electron volts. The presented one-dimensional (1D) model cannot describe exactly the electronic structure of the cuprates, however, it allows for qualitative description of the Cu—O system.

In the model, we include two kinds of interaction between electrons and the Cu—O bond stretching mode. The first one, off-diagonal Su-Schrieffer-Heeger (SSH) (Ref. 24) coupling, results from the dependence of the overlap integral between neighboring atoms on the interatomic distance. Since the active bands are built mainly of hybridized copper and oxygen orbitals, this coupling influences directly states close to the Fermi energy. The strength of this interaction may be estimated from the known scaling law

$t = t_0(1+u)^{-7/2}$, where u is the relative change in the Cu—O distance. For small u , it can be written in the linear form

$$t_i(u) = t - \alpha(u_{i+1} - u_i), \quad (2)$$

with $\alpha \cong 1.2$ eV/Å. Another type of coupling, the diagonal (Holstein²⁵) coupling, is connected with the shift in the Madelung potential on copper, when oxygen ions are displaced from equilibrium positions

$$\varepsilon_i(u) = \varepsilon_{i0} - \beta(u_{i+1} - u_{i-1}). \quad (3)$$

This energy shift has been estimated using the electronic band calculations, and for the breathing mode, the energy shift on Cu atom is about 1 eV when oxygen is displaced of 0.1 Å.²⁶ This coupling usually depends strongly on doping, and will be reduced with increasing x .

In this study, we use the adiabatic approximation ($t \gg \omega_{ph}$), in which phonons are treated as classical atomic displacements. Since the oxygen mass is much smaller than the copper mass, we assume that only oxygen ions are displaced and coppers remain in the equilibrium positions. At each instant, positions of oxygens are determined by the wave vector q : $u_i = u_0 \cos(qr_i)$. In this paper, we do not discuss other oxygen phonons, such as buckling²² and bending modes, or out-of-plane c -axis modes, which also couple to doped charges.²⁰

III. DYNAMIC CHARGE TRANSFER

We start the analysis of phonon-induced charge transfer by discussing the influence of lattice deformation on polarization in insulating materials, which is well understood. Displacement of atoms from equilibrium positions induces changes in charge density $\rho(r)$ and microscopic polarization field $P(r)$.

The induced polarization can be connected with the transient current due to ionic displacements, which flows through the system

$$\dot{P}(r,t) = j(r,t). \quad (4)$$

This current consists of the ionic part, which corresponds to rigid ion displacements, and the electronic part associated with the charge transfer between different ions. For a ferroelectric solid, the total integrated current is equal to the macroscopic polarization

$$\Delta P = \int dt dr j(t,r). \quad (5)$$

Since the current is associated with the phase of the wave function, the macroscopic polarization can be obtained using the Berry phase of the ground state.^{16,17} In insulators, the macroscopic polarization can vary continuously and sustains nonzero net values only in broken symmetry (ferroelectric) states ($q=0$). In this case, the electronic current (charge transfer) is parallel to ionic displacements, and the macroscopic polarization is enhanced. Consequently, the dynamic effective charge $Z^* = \Delta P/u$ can be much larger than the nominal ionic value.

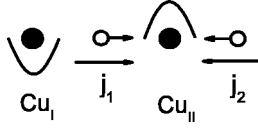


FIG. 1. Schematic of oxygen ion displacements in the half-breathing mode and directions of induced currents.

In this paper, we focus on the local polarization behavior in the metallic state for $q \neq 0$, using the method developed for correlated electron systems.^{27–29} In order to describe local charge transfer effects due to phonons, we introduce the induced microscopic polarization $\Delta P(r)$. In Ref. 30, the microscopic polarization, induced by external electric field, was calculated using the *ab initio* density functional approach. In general, the induced polarization can be written as the Fourier series

$$\Delta P(r) = \sum_q \Delta P_q e^{iqr}. \quad (6)$$

Since the polarization is connected with the charge density by the equation $\nabla P(r) = -\rho(r)$, the Fourier transforms have a linear dependence, $iq\Delta P_q = \Delta\rho_q$. Therefore, the staggered polarization ΔP_q describes the spatial modulation of the charge density induced by phonons. The macroscopic dynamic charge describes long-range effects. In order to describe short-range effects we introduce by analogy a q -dependent effective charge, defined as the derivative of the microscopic staggered polarization with respect to the atom displacement

$$Z_{\alpha}^*(q) = \lim_{u_{\alpha,q} \rightarrow 0} \frac{\Delta P_q}{u_{\alpha,q}}, \quad (7)$$

where $u_{\alpha,q}$ is the amplitude of atomic displacements. The first Fourier component for $q=0$ is the macroscopic polarization—the integrated polarization over the entire crystal

$$\Delta P = \frac{1}{V} \int \Delta P(r) dr = \Delta P_{q=0}, \quad (8)$$

and the dynamic effective charge coincides with the Born dynamic charge, $Z^*(q=0)$.³¹ However, at $q=0$ the integral depends upon the boundary conditions, and can be exactly evaluated only with the Berry phase formalism. Since the Berry phase cannot be defined for a metal, this quantity is ill defined in the present calculation. On the other hand the integral (7) gives the q -dependent polarization exactly, which conveniently describes the local charge transfer phenomenon and its q dependence.

In general, ΔP_q depends on the position in space, and the dynamical effective charge should be calculated by averaging the polarization over a unit cell. In our model the charge density is defined as an occupation number in a particular orbital $\rho_i = n_i$. Therefore, we can evaluate the charge transfer between ions directly by calculating the changes in static charges $\delta\rho_i$. As an example we discuss in detail the zone-boundary phonon mode, the breathing mode, which is schematically shown in Fig. 1. In this case, only oxygen ions are moving and in each instant they are displaced away from one

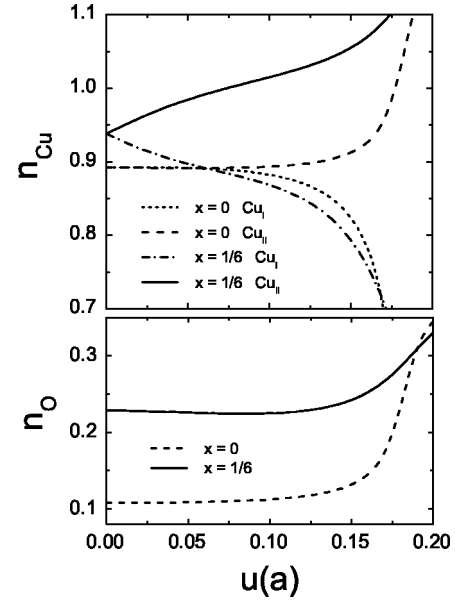


FIG. 2. Hole density on Cu and O atoms as a function of ion displacement u for the breathing mode and two doping concentrations $x=0$ and $1/6$.

copper (Cu_I) toward another copper (Cu_{II}). This displacement induces charge transfer between copper ions: Charge density increases (decreases) on copper Cu_{II} (Cu_I). There is also a change in the oxygen charge density. However, for this particular mode it is much smaller than the charge induced on copper ions, since most of charges flow through oxygen. Because of the mirror symmetry, two currents, which flow through adjacent cells are equal in magnitude and have opposite directions $j_1 = -j_2$. The induced polarization in this case changes the sign at each unit cell, creating instantaneously a staggered antiferroelectric state. The charges transported through adjacent cells are equal $\rho_1 = \rho_2 = \delta\rho/2$, where $\delta\rho = \delta n_{\text{Cu}}$ is the induced charge on copper Cu_{II} . It implies that $\Delta P_{\pi} = \delta\rho a/2$ and the dynamic effective charge of oxygen is given by

$$Z_0^*(\pi) = Z_{\text{ion}} + \lim_{u \rightarrow 0} \frac{\delta\rho a}{2u}, \quad (9)$$

where Z_{ion} is the ionic (static) charge of oxygen. As we see, the electronic part of the dynamic charge is simply the amount of charge transferred between Cu atoms, divided by the oxygen displacement u (in units of lattice constant). This procedure can be repeated for all phonon modes except for the $q=0$ zone-center mode. In doped CuO systems, the second term in Eq. (9) was found to have an opposite sign to Z_{ion} , and may be even larger in magnitude.

At half-filling ($x=0$), the ground state of the system is an insulator with one hole per unit cell. Because of a nonzero charge transfer gap $\Delta = \epsilon_p - \epsilon_d$ holes occupy mainly Cu $d_{x^2-y^2}$ orbitals and only a small fraction is located at O $p_{x/y}$ sites. When oxygen ions are displaced from equilibrium positions the static charges vary on both Cu and O atoms. Figure 2 presents the dependence of the hole density on Cu and O ions as a function of oxygen displacement u for the breathing

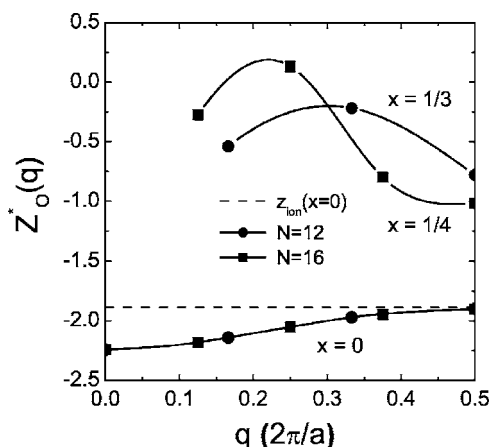


FIG. 3. Dependence of the dynamic effective charge of oxygen Z_0^* on q for the half-filling ($x=0$) and two doping levels $x=1/4$ and $1/3$.

mode, in the $N=12$ site system (six Cu and six O atoms). In the undoped system, strong electron correlations suppress charge fluctuations. Therefore for small atom displacements there is almost no change in the charge density. However, at some critical displacement ($u_c > 0.15$), a gain in the e - p interaction energy overcomes the Coulomb on-site energy, and there is a sudden change in charge density on copper and oxygen. As a consequence of charge transfer, a local magnetic moment on Cu atoms vanishes and the system undergoes phase transition between an antiferromagnetic insulator and a paramagnetic insulator.²⁸ It was demonstrated that the polarization changes discontinuously at this phase transition, and the Berry phase plays the role of the order parameter.^{28,29} It is interesting to note that the dynamic effective charge reverses its sign at the critical point: Oxygen transports positive and copper negative charge. However, in the cuprates, where U_d is large, this transition could occur only for very large atomic displacements, and the insulating state is always antiferromagnetic.

We have calculated the effective charge for the undoped state for $q=0$ using the Berry phase approach. Calculations were performed using the twisted boundary conditions with 40 k points in the Brillouin zone. For $\alpha=0$ the dynamic charge is equal to the ionic charge $Z_{ion} = -1.9$, and with increasing α , Z^* becomes more negative. The electronic current is parallel to the ionic current, and the polarization increases. However, unlike in ferroelectric materials, dynamic charge does not differ much from nominal charges, indicating that undoped cuprates have more ionic than covalent character. The values of Z_0^* for realistic e - p couplings agree with experimental values, $Z_0^* = 2.05 - 2.38$.³² The finite size effect on Z^* in the same model was studied in Ref. 29, and it was found to be very small. We have calculated Z_0^* for two systems, obtaining $Z_0^* = -2.241$ and -2.242 for $N=8$ and $N=12$, respectively. The effective charges calculated in the 1D system may be numerically different than in the 2D system, however, we do not expect significant qualitative changes. The q -dependent effective charge of an insulator is shown in Fig. 3 as a function of q . The q -dependence is weak. Interestingly the value of Z_0^* obtained directly from charge trans-

fer extrapolates in the limit $q \rightarrow 0$ nicely to the exact value calculated from the Berry phase.

Charge dynamics changes completely when the system is doped with holes. Doped holes go mainly to oxygen orbitals because of large Coulomb repulsion U_d on Cu atoms. When the breathing phonon mode is activated even small lattice displacement ($u < 0.05$) induces pronounced charge transfer between ions and charge density changes continuously with increasing u , as shown also in Fig. 2. Because of the symmetry of the breathing mode, the change of charge density on Cu ions is much larger than on O ions. Thus, the oxygen breathing mode induces dynamic charge density wave (CDW) on copper ions. For $q > 0$ the effective charge increases rapidly with α , becoming less negative, and above a certain critical value ($\alpha \cong 2$ eV/Å for $q = \pi$) it even changes the sign and becomes positive. In such a case oxygen effectively transports a positive charge.

In Fig. 3, we present the q dependence of Z_0^* for two doping concentrations $x=1/4$ and $1/3$. As we mentioned above the Berry phase method, which assumes the gap between the occupied and unoccupied states, is not valid for a doped metallic system, therefore, in Fig. 3 we plot Z_0^* only for $q > 0$. Z_0^* is much more strongly q dependent than in the case of the undoped insulator. Unlike the case of the half-filled system, Z_0^* quickly becomes less negative with increasing q , reaching a maximum value. The position of this maximum depends on the doping level and for $x=1/4$ it is in the middle of the Brillouin zone. This behavior may be considered as the Kohn anomaly, since the position of the maximum of the electronic polarization is related to $2k_F$ of non-interacting fermions.

The strong phonon-induced charge transfer shown here justifies characterizing the phonon-assisted charge transport as “vibronic.” If the effect of lattice becomes too strong, it will induce a static CDW state. In ferroelectrics the electronic polarization is parallel to the ionic polarization and increases the internal electric field, which promotes ferroelectricity. In the cuprate since they are antiparallel this effect is greatly weakened, and the near neighbor Coulomb interaction does not help phonon softening. Thus strong electron-phonon coupling is less likely to lead to CDW formation. Since static CDW or the static stripes will suppress superconductivity, as is observed in the Nd-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO),¹ this mechanism allows stronger e - p coupling without the CDW formation, the so-called covalency catastrophe of the BCS mechanism as discussed below.

The value of the q -dependent effective charge is to express the mechanism of electronic polarization effect more explicitly. For the half-breathing mode the actual charge of oxygen does not change much as shown in Fig. 2. Thus it appears that the charge transfer effect is small.³³ However, this is because for the half-breathing mode the charge transfer to oxygen from a copper ion on one side and the charge transfer from oxygen to another copper ion on the other side are nearly equal, thus the total charge transfer from the copper system to oxygen is small. But the actual charge transfer from one copper to the other through oxygen is large, and this charge transfer is caused by the Cu—O charge transfer. This effect can be expressed in terms of Z^* for oxygen.

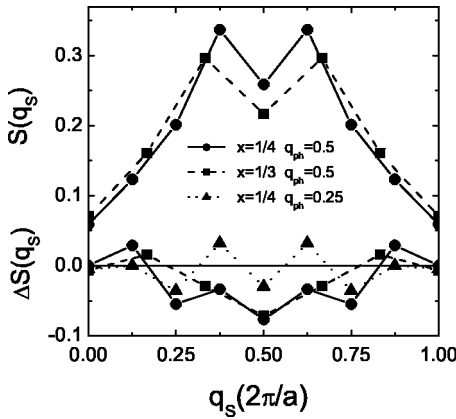


FIG. 4. Magnetic structure factor $S(q)$ for $x=1/4$ and $1/3$. In the lower part the effect of two phonon modes with $q_{ph}=0.25$ and 0.5 is presented.

IV. SPIN DYNAMICS

In this section, we study the influence of the charge transfer induced by phonons on magnetic states and spin dynamics. In undoped cuprates, strong electron correlations in the d states on Cu atoms result through the super-exchange mechanism in the antiferromagnetic state. After small doping, the magnetic moment on Cu rapidly decreases and the long-range order disappears. However, short-range spin correlations remain, and have been observed by inelastic neutron scattering (INS) measurements. The INS experiments revealed the low-energy incommensurate peaks at momenta $q=[\pi, \pi(1 \pm \delta)]$ and $q=[\pi(1 \pm \delta), \pi]$, where δ is the doping concentration.^{34–36} In the Nd-doped LSCO,¹ the incommensurate peaks are observed at the same positions by elastic scattering, indicating a long-range stripe order. In this case the spin-charge stripes are stabilized by the lattice through local deformations.³⁷ Thus it is likely that the e - p interaction influences the magnetic response of dynamic spin-charge fluctuations even when stripes are not stable.

While stripes can be described only in 2D models, the essential features of local spin fluctuations and incommensurability may be investigated using the 1D system. Static spin-spin correlations can be studied using the equal-time (instantaneous) magnetic structure factor defined as

$$S(q) = \langle 0 | S_{-q} S_q | 0 \rangle, \quad (10)$$

where $|0\rangle$ is the ground state and the spin operator $S_q = 1/N \sum_i \exp(iqr_i) S_i$, with $S_i = 1/2(n_{i\uparrow} - n_{i\downarrow})$. Figure 4 presents the static structure factor $S(q)$ obtained for $N=12$ and 16 with $x=1/3$ and $1/4$, respectively. $S(q)$ has a characteristic incommensurate structure with two peaks at momenta $q_{in} = \pi(1 \pm x)$. It should be noted that in the 1D electronic system a long-range order cannot exist, however, short-range correlations results in a similar magnetic response. In Fig. 4, the effect of phonons is demonstrated in the lower part of the graph. $\Delta S(q)$ is the difference in magnetic response between states with and without the e - p coupling. The strongest effect occurs at the zone boundary, where $S(q)$ decreases for both phonon modes with $q_{ph}=0.25$ and $q_{ph}=0.5$. This result implies that antiferromagnetic correlations are suppressed by

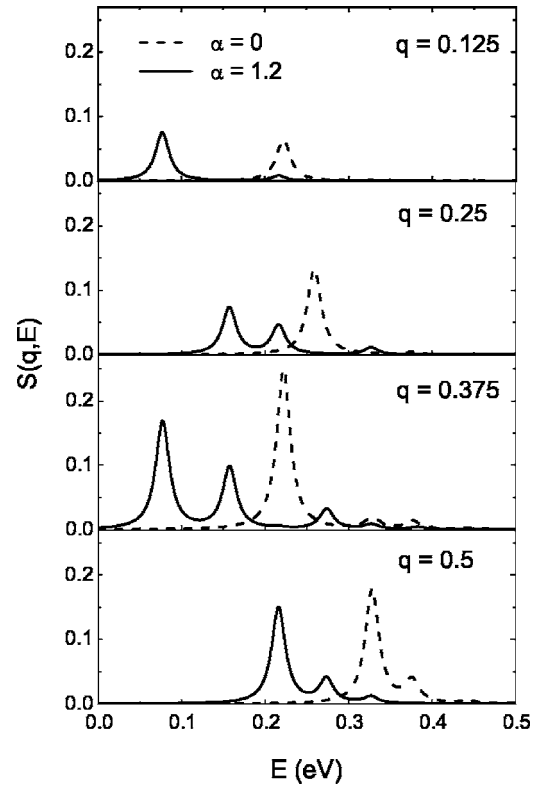


FIG. 5. Dynamic structure factor $S(q, \omega)$ calculated in the 16-site system ($x=1/4$) for $\alpha=0$ and 1.2 eV/Å with $u=0.1$ and $q_{ph}=0.5$.

coupling to the lattice. On the other hand the spin fluctuations are enhanced slightly at $q_{in}=0.375$ by the $q_{ph}=0.25$ phonon mode.

We now discuss the effect of phonons on spin dynamics. The spectral weight of spin excitations can be obtained from the dynamic structure factor

$$S(q, \omega) = \sum_n |\langle n | S_q | 0 \rangle|^2 \delta(\omega - E_n + E_0), \quad (11)$$

where summation is over all excited states $|n\rangle$ with energies E_n , and $|0\rangle$ is the ground state. In Fig. 5 we show the dynamic structure factor $S(q, \omega)$ for $N=16$ and $x=1/4$. The δ function in Eq. (11) is replaced by the Lorentzian with the width $\epsilon=0.01$ eV. The lowest excitation is at $q_{in}=0.375$ and is separated from the ground state by the spin gap $\Delta_s \cong 0.22$ eV. There is also a significant spectral weight at $q=0.5$, indicating the presence of dynamic antiferromagnetic correlations. In Fig. 5 we present also the effect of the covalent e - p coupling α on $S(q, E)$. As we see the lowest energies of spin excitations strongly soften, when electrons are coupled to the lattice. The largest change in energy is at q_{in} , where the spin gap is reduced to $\Delta_s=77$ meV. Additionally, the maximum at q_{in} splits into two peaks, and the spectral weight of the lowest excitation is decreased. We expect that two kinds of the e - p coupling, covalent and ionic, will produce different effects on spin dynamics. Also, as the spin-phonon interaction is a consequence of charge transfer, it may depend on the phonon wave vector. In Fig. 6, we plot

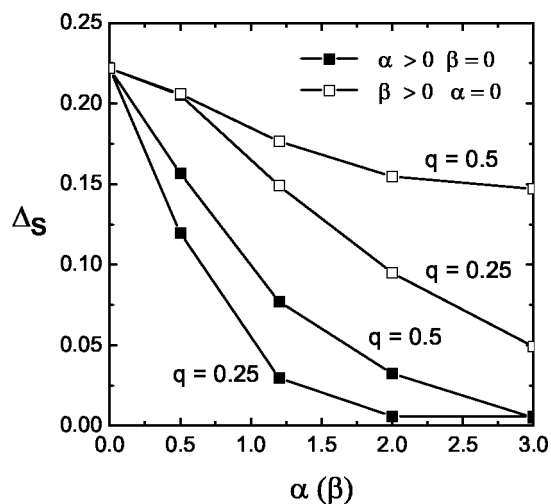


FIG. 6. Dependence of the spin gap Δ_s on the e - p couplings α and β for two phonon modes $q_{ph}=0.25$ and 0.5 .

the dependence of Δ_s on two e - p coupling constants, α and β , and two phonon wave vectors $q_{ph}=0.5$ and $q_{ph}=0.25$. With an increase in the e - p coupling, $\Delta_s \rightarrow 0$, indicating the transition from the short-range correlated state to long-range order with the wave vector q_{in} . Comparing two phonon modes, we observe a stronger effect for $q_{ph}=0.25$ than for $q_{ph}=0.5$. This must be related to the q dependence of charge transfer, which is maximum at $q_{ph}=0.25$ for doping concentration $x=1/4$. The result presented in Fig. 6 also demonstrates that the influence of the covalent coupling is stronger than the ionic coupling, in agreement with previous studies.^{6,18}

In this type of calculation, the size effect is the most crucial source of uncertainty. In the doped system, it is difficult to control finite size effects, since the doping depends on the number of sites. For instance, the calculated spin gap is much larger than experimental values observed in the cuprates. Comparing the results from 12- and 16-site systems, we see a decrease in the spin gap with increasing N , however, we have too few points to perform finite size scaling. A difference between the calculated and observed values of the spin gap may result also from the one dimensionality of the model. Therefore, the presented results have to be treated qualitatively rather than as exact solutions.

Recently, the spin-phonon interaction was studied using the density functional band calculations,³⁸ and it was shown that the local exchange interaction and magnetic moment depend on the lattice deformation around the Cu site. It was suggested that the coupling between phonons and spin waves may decrease the frequency of spin excitations to phonon frequencies, thus enhancing the pairing of holes. Since the band calculations largely underestimate electron correlations and magnetic moments, the spin-phonon coupling in a real material may even be stronger. Indeed a more recent quantum Monte Carlo calculation on two-dimensional three-band Hubbard model³³ shows strong spin-phonon coupling for the half-breathing mode.

V. OPTICAL CONDUCTIVITY

Optical measurements provide useful information about the electronic excitations and transport properties of materi-

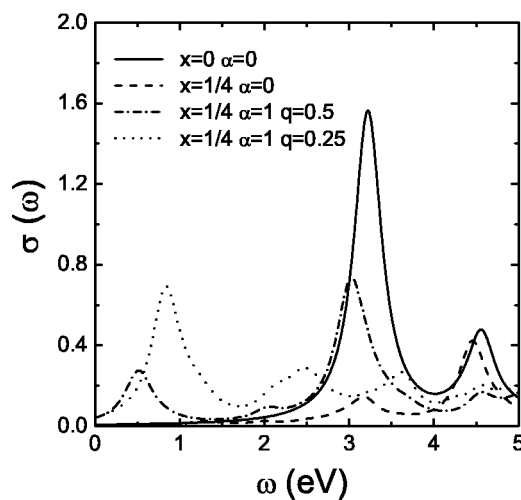


FIG. 7. Optical conductivity calculated for $x=0$ and $x=1/4$. The figure presents also the effect of two phonon modes $q_{ph}=0.25$ and 0.5 for $u=0.1$.

als. In the undoped cuprates, optical conductivity shows absorption spectra characteristic to insulating materials with the charge-transfer gap of about 2 eV. After doping, the spectral weight is transferred to lower energies, creating the midinfrared (MIR) band at ~ 0.5 eV, and the Drude peak develops at zero energy. The optical conductivity has been calculated using the exact diagonalization method in the 1D and 2D Hubbard models.³⁹⁻⁴¹ In 2D models, the optical conductivity shows a broad MIR band above the Drude peak, in qualitative agreement with the experiment. This band results from the interaction between doped holes and the antiferromagnetic spin background. In contrast, in 1D models there is almost no spectral weight at finite frequencies apart from the Drude peak, due to spin and charge separation.³⁹ The situation changes greatly, however, when the electronic system is coupled to the lattice. The numerical studies of the 1D two-band Hubbard-Peierls model within the Hartree-Fock approximation showed that the sliding motion of CDW and spin density wave (SDW) produces low-energy collective modes in the infrared regime.⁴² The exact diagonalization calculations in 2D Holstein t - J model¹⁹ confirmed a significant modification of the low-energy optical absorption as a result of the lattice polaron formation. In the preceding section, we observed that the e - p interaction modify strongly the lowest spin excitations. Now, we will investigate the effect of the phonon-assisted charge transfer on the optical conductivity spectrum.

The regular part of the optical conductivity at $T=0$ is given by the expression

$$\sigma(\omega) = \frac{\pi}{N} \sum_n \frac{|<0|j|n>|^2}{E_n - E_0} \delta(\omega - E_n + E_0), \quad (12)$$

where the current operator is defined as

$$j = -iet_{pd}(u) \sum_{i\sigma} (d_{i,\sigma}^\dagger p_{i+1,\sigma} - p_{i+1,\sigma}^\dagger d_{i,\sigma}). \quad (13)$$

Figure 7 presents the optical conductivity calculated for the

undoped and doped ($x=1/4$) systems. In order to simulate the effects which contribute to the broadening of peaks in $\sigma(\omega)$ we use Lorentzians with large $\epsilon=0.2$ eV. At half-filling, there is a charge-transfer band above the optical gap $\Delta \approx 3$ eV. After doping the intensity of this charge-transfer band decreases indicating the insulator-to-metal transition. Note that the Drude peak is not included in Fig. 7. In the undistorted system ($\alpha=0$), there is no spectral weight at low energies, in agreement with previous calculations.³⁹ However, in the distorted state with broken symmetry, the excitation states show up in the infrared region. This low-energy band involves collective excitations of the CDW states induced by phonons. The breathing phonon mode ($q=0.5$), which corresponds to the CDW with $2a$ periodicity, generates an absorption band around 0.5 eV and additionally enhances charge transfer above the optical gap. The midzone phonon mode ($q=0.25$) induces a spectral weight at around 1 eV with larger intensity than the breathing mode. The explanation is the same as for the spin-phonon coupling. For this particular doping $x=1/4$, the midzone mode produces larger charge transfer than the breathing mode (see Fig. 3). Changing doping will modify the spectral weight in the MIR band and shift the position of the maximum.

The present result demonstrates that the e - p coupling may contribute to the MIR absorption band. As we mentioned before, in 2D systems spin excitations are likely to contribute as well. A recent study of the three-band model of the CuO_2 planes showed that stripes produce the MIR band, and the position of this band depends on doping,⁴³ in qualitative agreement with the experiment.

VI. DISCUSSION

The e - p coupling shown here is quite different from those for the free-electron systems. The behavior of the dynamic effective charge of the doped system at $q>0$ is in stark contrast to that of the ferroelectric systems. In the ferroelectric solids the dynamic effective charge is much larger than the static charge, and the static charge is reduced by increased covalency when TM-O distance is reduced. Consequently the LO phonon mode is hardened, while the TO mode is softened, leading to the divergence of the $\omega_{\text{LO}}/\omega_{\text{TO}}$ ratio and the static dielectric constant through the Lyddane-Sachs-Teller relationship, at the ferroelectric transition. In contrast in the cuprates the phonon-induced charge transfer increases ionicity when the Cu—O distance is reduced, and softens the LO phonon.

It is interesting to speculate on the implications of the observed results. The in-plane Cu—O bond-stretching LO phonon modes are known to show strong softening near the zone-boundary upon doping,^{3,4} but recent data indicate that the accompanying TO modes do not show softening at all.⁹ This behavior is a complete opposite of the TO mode softening observed for ferroelectric materials as mentioned above. It is difficult to explain this behavior with the regular lattice dynamics without invoking counter-intuitive parameters, such as oxygen-oxygen attraction only in one direction,⁴ and it most likely has to be explained in terms of the electronic effect. The charge transfer effect of the LO

phonons near the zone-boundary shown here leads to phonon softening,¹⁴ and thus could offer a likely explanation of the softening observed for the cuprates.

The difficulties in the lattice dynamics calculations for the cuprates result from the nature of the strongly correlated electronic state in these materials. Since the *ab initio* density functional method cannot describe properly the insulating state, the doping dependence of the phonon spectra cannot be explained within this approach. Using a quasi-*ab initio* approach, Falter and Hoffmann⁴⁴ considered the ionic model with phonon-induced charge fluctuations between outer ionic shells. They showed that this nonlocal e - p coupling leads to softening of the LO optical modes at the zone boundary.

Some other approaches take into account the influence of electron correlations. Using the t - J model, it was demonstrated that anomalous softening and broadening may be explained by the coupling between phonons and low-energy charge density fluctuations.⁴⁵ Recently, the doping-induced phonon softening was studied in the t - J model by the slave-boson⁴⁶ and exact diagonalization technique.⁴⁷ Park and Sachdev⁴⁸ showed that the influence of the dynamically fluctuating spin-Peierls order parameter on bond-stretching mode leads to anomalous discontinuity in the phonon dispersion. The phonon softening was studied also in a simple mechanical model in which a “negative” spring constant between oxygens was considered.⁴ The dynamic charge transfer studied in this paper may be considered as the microscopic origin of the negative spring constant. When positive charge is transported between ions as a result of oxygen displacement, additional attractive interaction between copper and oxygen ions is generated. Since only oxygen ions are moving in the breathing mode, this additional Coulomb force may be treated as an effective attractive interaction between oxygen ions.

The strong effects of phonon modes on the charge and spin excitations shown here are quite different from those of free electron systems upon which the BCS theory of superconductivity is based, and appear to compel the reexamination of the role of phonons in the superconductivity of the cuprates. A possible limitation of T_c in the phonon mechanism of superconductivity was discussed in the past.⁴⁹ It was claimed that a strong e - p coupling will lead to charge ordering and lattice instability rather than a high- T_c superconductivity. This conclusion was based on the assumption that the dielectric function must fulfill the condition $\epsilon_{\text{tot}}(\mathbf{k}, \omega) > 0$. However, it was demonstrated that $\epsilon_{\text{tot}}(\mathbf{k}, \omega)$ can be negative for large values of \mathbf{k} when exchange and correlations effects are taken into account.⁵⁰ The present calculation shows that for some wave vectors \mathbf{k} the electronic polarization is opposite in sign and comparable in magnitude to the lattice polarization, suggesting the possibility of overscreening of lattice polarization by electronic polarization, not by electrostatic screening but by charge transfer. However, the total polarization is too small to demonstrate the amplification effect expected in the overscreening mechanism of superconductivity.^{51,52} As noted by Kulić,²¹ local field effects in the cuprates may modify significantly dielectric properties and give rise to large e - p coupling. Using similar arguments, Weger and Birman⁵³ demonstrated that nondiagonal elements of the ionic dielectric function significantly enhance the phonon mechanism of superconductivity.

We have also demonstrated that phonons can have a strong effect on optical conductivity up to the energy range much higher than the phonon energy. This is because the LO phonons modify t through the SSH coupling, and modifies the entire band structure, not just the vicinity of the Fermi surface. It was found the change in the optical conductivity due to Cooper pair formation extends to high frequencies, and this was interpreted to signify an electronic mechanism of pairing.^{54–56} The present calculation suggests that the e - p coupling may explain the observed effect, and the phonon mechanism of pairing may still be consistent with the observation.

VII. CONCLUSION

The main aim of this paper is to examine the influence of the e - p interaction on spin-charge system in the doped cuprates. We have shown that in the strongly correlated system the e - p interaction produces effects, which do not appear in simple metals. In particular, we have demonstrated that the energy spectra of spin excitations and optical conductivity are strongly influenced by lattice distortions. These results suggest that while the conventional phonon mechanism

(BCS theory) does not explain the high-temperature superconductivity, the e - p coupling in the cuprates is unconventional and it may still be premature to discard it from consideration for the pairing mechanism. Due to strong electron correlations phonons are strongly dressed by spin and charge. This may result in a synergetic pairing mechanism of spin, charge, and lattice.

In the present paper, spin dynamics, which results from electron correlations, was fully taken into account, while phonons were treated as static strains. Since both spin waves and phonons have similar excitation energies, we expect nonadiabatic effects to emerge when phonons are treated dynamically. It is our view that the phonon mechanism of pairing should not be abandoned until such a nonadiabatic theory, yet to be fully formulated, is found to be insufficient to explain the high-temperature superconductivity.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation through DMR01-02565 and DMR04-04781. The authors acknowledge useful discussions with R. Resta, D. Vanderbilt, M. Tachiki, S. Ishihara, A. Bishop, N. Bontemps, A. Bussmann-Holder, and L. Gor'kov.

-
- ¹J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, *Nature (London)* **375**, 561 (1995).
- ²T. Egami and S. J. L. Billinge, in *Physical Properties of High Temperature Superconductors V*, edited by D. Ginsberg (Singapore, World Scientific, 1996) p. 265.
- ³L. Pintschovius, N. Pyka, W. Reichardt, A. Yu. Rumiantsev, N. L. Mitrofanov, A. S. Ivanov, G. Collin, and P. Bourges, *Physica C* **185**, 156 (1991).
- ⁴R. J. McQueeney, Y. Petrov, T. Egami, M. Yethiraj, G. Shirane, and Y. Endoh, *Phys. Rev. Lett.* **82**, 628 (1999).
- ⁵A. Lanzara, P. V. Bogdanov, X. J. Zhou, S. A. Keller, D. L. Feng, E. D. Lu, W. J. Zheng, G. Gu, J.-I. Shimoyama, K. Kishio, H. Ikeda, R. Yoshizaki, Z. Hussain, and Z.-X. Shen, *Nature (London)* **412**, 510 (2001).
- ⁶Z.-X. Shen, A. Lanzara, S. Ishihara, and N. Nagaosa, *Philos. Mag. B* **82**, 1349 (2002).
- ⁷G.-M. Zhao, M. B. Hunt, H. Keller, and K. A. Müller, *Nature (London)* **385**, 236 (1997).
- ⁸R. Khasanov, A. Shengelaya, K. Conder, E. Morenzoni, I. M. Savić, and H. Keller, *J. Phys.: Condens. Matter* **15**, L17 (2003).
- ⁹J.-H. Chung, T. Egami, R. J. McQueeney, M. Yethiraj, M. Arai, T. Yokoo, Y. Petrov, H. A. Mook, Y. Endoh, S. Tajima, C. Frost, and F. Dogan, *Phys. Rev. B* **67**, 014517 (2003).
- ¹⁰E.g., A. Bianconi, N. L. Saini, A. Lanzara, M. Missori, T. Rossetti, H. Oyanagi, H. Yamaguchi, K. Oka, and T. Ito *Phys. Rev. Lett.* **76**, 3412 (1996).
- ¹¹E.g., E. S. Bozin, G. H. Kwei, H. Takagi, and S. J. L. Billinge, *Phys. Rev. Lett.* **84**, 5856 (2000).
- ¹²T. Egami, in *Intrinsic Multiscale Structure and Dynamics*, edited by A. R. Bishop, S. R. Shenoy, and S. Sridhar (Singapore, World Scientific, 2003) p. 213.
- ¹³T. Egami, S. Ishihara, and M. Tachiki, *Science* **261**, 1307 (1993).
- ¹⁴S. Ishihara, T. Egami, and M. Tachiki, *Phys. Rev. B* **55**, 3163 (1997).
- ¹⁵R. Resta, *Ferroelectrics* **136**, 51 (1992).
- ¹⁶R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B* **47**, R1651 (1993).
- ¹⁷R. Resta, *Rev. Mod. Phys.* **66**, 899 (1994).
- ¹⁸K. Yonemitsu, A. R. Bishop, and J. Lorenzana, *Phys. Rev. Lett.* **69**, 965 (1992); *Phys. Rev. B* **47**, 12059 (1993).
- ¹⁹B. Bäuml, G. Wellein, and H. Fehske, *Phys. Rev. B* **58**, 3663 (1998).
- ²⁰A. Bussmann-Holder, K. A. Müller, R. Micnas, H. Büttner, A. Simon, A. R. Bishop, and T. Egami, *J. Phys.: Condens. Matter* **13**, L169 (2001).
- ²¹M. L. Kulić, *Phys. Rep.* **338**, 1 (2000).
- ²²P. Piekarz, J. Konior, and J. H. Jefferson, *Phys. Rev. B* **59** 14697 (1999); P. Piekarz and J. Konior, *ibid.* **63** 214517 (2001).
- ²³R. L. Martin, *Phys. Rev. B* **53**, 15501 (1996).
- ²⁴W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **42**, 1698 (1979).
- ²⁵T. Holstein, *Ann. Phys.* **8**, 325 (1959).
- ²⁶T. Jarlborg and G. Santi, *Physica C* **329**, 243 (2000).
- ²⁷G. Ortiz and R. M. Martin, *Phys. Rev. B* **49**, 14202 (1994).
- ²⁸R. Resta and S. Sorella, *Phys. Rev. Lett.* **74**, 4738 (1995).
- ²⁹G. Ortiz, P. Ordejon, R. M. Martin, and G. Chiappe, *Phys. Rev. B* **54**, 13515 (1996).
- ³⁰P. Umari, A. Dal Corso, and R. Resta, *Fundamental Physics of Ferroelectrics: 2001 Williamsburg Workshop*, edited by H. Krakauer (AIP, Woodbury, New York), p.107.
- ³¹R. M. Pick, M. H. Cohen, and R. M. Martin, *Phys. Rev. B* **1**, 910 (1970).

- ³²S. Tajima, T. Ido, S. Ishibashi, T. Itoh, H. Eisaki, Y. Mizuo, T. Arima, H. Takagi, and S. Uchida, *Phys. Rev. B* **43**, 10496 (1991).
- ³³Z. B. Huang, W. Hanke, and E. Arrighoni, cond-mat/0309380 (unpublished).
- ³⁴H. A. Mook, Pengcheng Dai, S. M. Hayden, G. Aeppli, T. G. Perring, and F. Dogan, *Nature (London)* **395**, 580 (1998).
- ³⁵M. Arai, T. Nishijima, Y. Endoh, T. Egami, S. Tajima, K. Tomimoto, Y. Shiohara, M. Takahashi, A. Garrett, and S. M. Bennington, *Phys. Rev. Lett.* **83**, 608 (1999).
- ³⁶H. A. Mook, Pengcheng Dai, F. Dogan, and R. D. Hunt, *Nature (London)* **404**, 729 (2000).
- ³⁷T. Egami and D. Louca, *Phys. Rev. B* **65**, 094422 (2002).
- ³⁸T. Jarlborg, *Phys. Lett. A* **295**, 172501 (2002); *Phys. Rev. B* **68**, 172501 (2003).
- ³⁹W. Stephan and P. Horsch, *Phys. Rev. B* **42**, R8736 (1990).
- ⁴⁰E. Dagotto, *Rev. Mod. Phys.* **66**, 763 (1994).
- ⁴¹J. Wagner, W. Hanke, and D. J. Scalapino, *Phys. Rev. B* **43**, 10517 (1991).
- ⁴²K. Yonemitsu and A. R. Bishop, *Phys. Rev. B* **48**, 3349 (1993).
- ⁴³J. Lorenzana and G. Seibold, *Phys. Rev. Lett.* **90**, 066404 (2003).
- ⁴⁴C. Falter and G. A. Hoffmann, *Phys. Rev. B* **61**, 14537 (2000); **64**, 054516 (2001).
- ⁴⁵G. Khaliullin and P. Horsch, *Physica C* **282-287**, 1751 (1997).
- ⁴⁶S. Ishihara and N. Nagaosa, *Phys. Rev. B* **69**, 144520 (2004).
- ⁴⁷O. Rösch and O. Gunnarsson, *Phys. Rev. Lett.* **92**, 146403 (2004).
- ⁴⁸K. Park and S. Sachdev, *Phys. Rev. B* **64**, 184510 (2001).
- ⁴⁹M. L. Cohen, P. W. Anderson, in *Superconductivity in d and f Band Metals*, edited by D. H. Douglass (AIP, New York, 1972), p. 17.
- ⁵⁰O. V. Dolgov, D. A. Kirzhnits, and E. G. Maksimov, *Rev. Mod. Phys.* **53**, 81 (1981).
- ⁵¹M. Tachiki and S. Takahashi, *Phys. Rev. B* **38**, 218 (1988); **39**, 293 (1989).
- ⁵²M. Tachiki, M. Machida, and T. Egami, *Phys. Rev. B* **67**, 174506 (2003).
- ⁵³M. Weger and J. I. Birman, *Laser Phys.* **12**, 1 (2002).
- ⁵⁴D. N. Basov, E. J. Singley, and S. V. Dordevic, *Phys. Rev. B* **65**, 054516 (2002).
- ⁵⁵H. J. A. Molegraaf, C. Presura, D. van der Marel, P. H. Kes, and M. Li, *Science* **295**, 2239 (2002).
- ⁵⁶A. F. Santander-Syro, R. P. S. M. Lobo, N. Bontemps, Z. Konstantinovic, Z. Z. Li, and H. Raffy, *Europhys. Lett.* **62**, 568 (2003).